X

OP- 1711

Assistant Commissioner for Patents
Washington, DC 20231
ATTENTION: Office of Petitions
Crystal Park 1, Room 520

RECEIVED

APR 2 9 1999

PROTEST UNDER 37 CFR 1.291(a)

GROUP 1700

April 23, 1999

Name of Applicant: Roland E. Stefandl
Application serial number: 08/802,202
Filing date of application: February 18, 1997
Title of Invention: Carpet Recycling Process for Nylon Containing Carpet
Current status of application: Pending

The undersigned hereby files this Protest under 37 CFR 1.291(a) with regard to pending US patent application 08/802,202. This application is cited as the priority data in International Publication Number WO 98/35998, published August 20, 1998. Having reviewed the World Search Report therein, the undersigned believes there are additional prior art documents with direct relevancy to the patentability of the disclosure of US patent application 08/802,202.

USP 5,430,068 to Subramanian and USP 5,280,105 to Moran each anticipate the broadest claimed invention as summarized in the following claims charts.

WO 98/35998 Inv. Stefandl Independent Claim 1:	USP 5,430,068 to Subramanian	USP 5,280,105 to Moran	USP 5,278,282 to Nauman and Lynch	CZ 143,502 to Petru et al.
Process for recycling of waste carpeting and waste carpeting containing materials which comprises	Col. 1, lines 53-58	Col. 1, lines 36-39	Col. 1, lines 20-29; Col. 5, lines 5-8	p.1, 1st sentence of 1st paragraph of text
a) multiple separation steps using selective solvents under controlled	Col. 1, lines 65-67; Col. 2, lines 2-3 and 13-16	Col. 1, lines 17-28	Col. 2, lines 54-64; Col. 6, lines 6-8; Figs. 1 and 2; Claims 1 and 5	p.3 line 12 through p. 4 line 12; p. 8, Ex. 3

temperature conditions				
b) which steps include selective stepwise separation and recovery of carpet backing, adhesives, and individual types and compositions of fibers present.	Col. 2, lines 26-31	Col. 2, lines 21-40 and lines 43-64 selective separation of N6 and N66; Col. 3, lines 32-33 nylon separated completely from backing, etc	Col. 6, liens 4-5 and lines 8-14	p.4, lines 13-23

WO 98/35998 Inv. Stefandl Independent claim 15:	USP 5,430,068 to Subramanian	USP 5,280,105 to Moran	USP 5,278,282 to Nauman and Lynch	CZ 143,502 to Petru et al.
The recovered nylon polymer obtained by the recycling steps for carpeting as described in Claim 1.		Col. 2, lines 37-40 (recovered nylon 6 product) and lines 60-64 (dried nylon 6,6 precipitate)	Col. 6, lines 11-14	p.4, lines 24-29; p. 8, Ex. 3

Both USP 5,430,068 and USP 5,280,105 teach methods explicitly intended for use on carpet waste of selective dissolution of component polymers using specific solvents and elevated temperature, and separating the dissolved polymer from the undissolved materials. Both teachings utilize carpet samples in their examples of their teachings (example 3 for USP 5,430,068 and examples 3 and 4 in USP 5,280,105). Both teach the use of temperature reduction to precipitate separated polymer as a means of recovering the separated polymer.

The obviousness of the claimed invention is established by USP 5, 278,282 to Nauman and Lynch. USP 5, 278,282 teaches a method of polymer reclamation for a mixed waste stream of plastics using a controlled sequence of solvents and temperatures to achieve selective dissolution, filtration to remove insoluble contaminates, and can yield separated polymers which "exhibit near first pass physical properties for marketing" (col. 5, lines 38-60). The method is intended for a wide array of commingled plastics including for instance: polyesters, polyolefins, polyvinyl derivative and polyamides (col. 16, lines 61-65). Application of this process to carpet waste is strongly suggested in the phrase "commingled, post-consumer plastics that result when plastics are separated from ordinary household trash" (col 1, lines 27-28). In Table 7, a mixture of nylon 6, polyethylene terephthalate (PET), and

polyvinylchloride (PVC) is selectively separated into the three polymer components using N,N Dimethyl Acetamide as the solvent and three different temperatures.

Czechoslovakian Patent 143,502 also establishes the obviousness of the claimed invention. This patent teaches a "method for producing caprolactam from waste consisting of a mixture of polycaprolactam and a noncaprolactam component", with the goal of achieving a reclaimed polymer which can be processed into "a high-quality, valuable product" (p. 1, 1st sentence of 1st paragraph and p. 2, lines1-4). One skilled in the art knows that carpet commonly comprises nylon 6 (polycaprolactam) and noncaprolactam components and thus, application of this method to carpet waste is strongly suggested by this statement. The method utilizes selective dissolution of the caprolactam in any known polycaprolactam solvent, either at room temperature or elevated temperature, depending on the solvent used. The noncaprolactam component may be separated from the dissolved polycaprolactam solution by filtration. The dissolved polycaprolactam may be recovered by cooling to cause precipitation.

Re: claim 2, based on col. 1, lines 36-39 of USP 5,280,105, a person skilled in the art would be led to substitute known separation techniques such in USP 5,518,188.
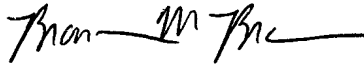
Re: claims 5,6 and 8, combination of USP 5,280,105 and USP 5,278,282 results in these claimed limitations. In addition, USP 5,241,066 to Davis and Dellinger separate the polycaprolactam sheath from the PET core in bicomponent fibers using selective dissolution and filtration.

Re: claim 9, Czechoslovakian Patent 143,502 demonstrates the separation of caprolactam fiber from cotton fiber by selective dissolution in Example 3, page 8 of the translation.

Re: claims 11, 12, 13 and 14, the fact that glycerol, ethylene glycol and propylene glycol are excellent solvents at elevated temperature for polyamide was established well prior to the claimed invention. In Starkweather, H. W. and Glover, A. J. (1981) "Crystalline Transitions in Powders of Nylon 66 Crystallized from Solutions", J. Polymer Sci. 19: 467-477, to avoid elevated pressure while dissolving nylon 66, a number of high boiling solvents were tested. Table I (p. 468) lists these solvents for nylon 66 in order of decreasing solubility parameter; glycerol, ethylene glycol, and propylene glycol are the top three solvents for dissolving nylon 66 at elevated temperature. This work also demonstrates the precipitation of dissolved polyamide by the use of reduced temperature. One skilled in the art of polymer dissolution would likely consult this article in trying to reclaim polymer components of polyamide carpet waste via dissolution.

In conclusion, this protest is filed to bring these highly relevant prior art documents to the Examiner's attention, which documents make the grant of the pending patent improper in the opinion of the undersigned.

Respectfully submitted,

Bronwen M. Brown
Reg. No. 43, 516
1115 Maryland Ave., NE
Washington, DC 20002
202-546-8016

Attached items:

1. Information Disclosure Statement
2. Cited references

Certificate of Service

I hereby certify that this correspondence (76 pages) was transmitted by first class mail to the agent of record, Joseph M. Skerpon et al. at Banner & Witcoff, Ltd., 11th Floor, 1001 G Street, N.W., Washington, DC 20001-4597 on April 23, 1999.

Bronwen M. Brown

Please type a plus sign (+) inside this box →

PTO/SB/08A (10-96)
Approved for use through 10/31/99. OMB 0651-0031
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Substitute for form 1449A/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(use as many sheets as necessary)

	Complete if Known	
Application Number	08/802,202	
Filing Date	Feb. 18, 1997	
First Named Inventor	Roland E. Stefandl	
Group Art Unit		
Examiner Name		

Sheet	1	of	2	Attorney Docket Number	

U.S. PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	U.S. Patent Document Number	Kind Code[2] (if known)	Name of Patentee or Applicant of Cited Document	Date of Publication of Cited Document MM-DD-YYYY	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		5,430,068		Subramanian, P.M.	7-04-1995	
		5,280,105		Moran, E.F.	1-18-1994	
		5,278,282		Nauman, E.B. et al	1-11-1994	
		5,518,188		Sharer, P.C.	5-21-1996	
		5,241,066		Davis, E.A. et al	8-31-1993	

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No.[1]	Foreign Patent Document Office[3]	Number[4]	Kind Code[5] (if known)	Name of Patentee or Applicant of Cited Document	Date of Publication of Cited Document MM-DD-YYYY	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T[6]
		WO	98/35998		Stefandl,R.E.	8-20-1998		
		CZ	143,502		Petru,K. et al	11-15-1971		X

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] Unique citation designation number. [2] See attached Kinds of U.S. Patent Documents. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST 16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

Burden Hour Statement: This form is estimated to take 2.0 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington, DC 20231.

PTO/SB/08B (10-96)
Approved for use through 10/31/99. OMB 0651-0031
Patent and Trademark Office: U.S. DEPARTMENT OF COMMERCE

Substitute for form 1449B/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(use as many sheets as necessary)

Complete if Known	
Application Number	08/802,202
Filing Date	Feb. 18, 1997
First Named Inventor	Roland E. Stefandl
Group Art Unit	
Examiner Name	
Attorney Docket Number	

| | Sheet | 2 | of | 2 |

OTHER PRIOR ART -- NON PATENT LITERATURE DOCUMENTS			
Examiner Initials*	Cite No.[1]	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	T[2]
		STARKWEATHER,H.W. and JONES,G.A. "Crystalline Transitions in Powders of Nylon 66 Crystallized from Solution" Journal of Polymer Science: Polymer Physics Ed. 1981 pp.467-477 Vol.19	

Examiner Signature		Date Considered	

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] : C08F 6/00, C08J 3/00, C08G 69/08, 73/10	A1	(11) International Publication Number: **WO 98/35998**
		(43) International Publication Date: 20 August 1998 (20.08.98)

(21) International Application Number: PCT/US98/03214

(22) International Filing Date: 18 February 1998 (18.02.98)

(30) Priority Data:
08/802,202   18 February 1997 (18.02.97)   US

(71)(72) Applicant and Inventor: STEFANDL, Roland, E. [US/US]; 62 Cider Hill, Upper Saddle River, NJ 07458 (US).

(74) Agents: SKERPON, Joseph, M. et al.; Banner & Witcoff, Ltd., 11th floor, 1001 G Street, N.W., Washington, DC 20001–4597 (US).

(81) Designated States: AU, BR, CA, CN, IL, JP, MX, RU, UA, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: CARPET RECYCLING PROCESS FOR NYLON CONTAINING CARPETING

(57) Abstract

This invention comprises recycling and recovery processes for rugs, flooring, carpeting, carpet materials, and all other textiles particularly from waste carpet containing both synthetic and natural fibers and for backing materials, and more particularly for the separation and recovery of various nylon polymers as well as other polymeric fibers and materials for recovery and reuse.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

CARPET RECYCLING PROCESS FOR NYLON CONTAINING CARPETING
FIELD of the INVENTION

The invention comprises methods and processes for recycling nylon
containing carpeting which includes stepwise separation using a
combination of selective solvent or solvents and temperatures control
methods. The steps include but are not limited to:

    a.   reduce carpet size to granular form;

    b.   wash and/or filter as necessary to remove inert
solids, dirt and fillers; and

    c.   stepwise separation of backing, adhesive and
various types of fibers.

BACKGROUND of the INVENTION

The use of synthetic fibers has increased in many areas of
technology. Among those areas which has had a very great and varied
increase is carpets, area rugs, carpeting and include all types of floor
coverings. The teachings and publications in this and related fields are
quite extensive and describe details for separating, reconstituting,

recovering, purifying and variously treating and handling used textiles and carpeting and include natural and synthetic fibers in the processing and recovery steps.

More specifically, U.S. Patent Number 3,006,867 (Simon) discloses a method of reconstituting a synthetic plastic, such as and including nylon from waste and used materials and include textile wastes having nylon fibers. The method consists of dissolving the waste material from the synthetic plastic in formic acid, mixing a hydrocarbon selected from n-hexane, cyclohexene, n-heptane, cyclohexane, hexene, benzene, and toluene with the formic acid-plastic solution in an amount sufficient to form an azeotropic mixture, then heating the azeotropic mixture to a temperature sufficient to vaporize the azeotropic mixture and removing (recovering) the vapors from the distillation zone to leave behind the desired synthetic plastic being recovered.

U.S. Patent Number 4,003,880; 4,003,881; 4,118,187 and 4,137,393 (Sidebotham et al) variously disclose methods for recovering polyester from dyed polyester fibers as in fabrics, textiles, carpeting and commercial products. Only polyesters are involved in the recovery steps. While the conditions and procedural steps vary in the patent disclosures, there are

2

certain steps which are described in and utilized in all these patent processes. These steps generally include:

1. contacting collections of yarns, fibers, and fabrics, including dyed polyester fibers with a dye-stripping solvent for polyester polymer which is preferably not a solvent for the remaining constituents at a temperature below which the polyester fiber dissolves and above the crystal lattice of the polyester fibers swell to as to release the dye, thereby stripping the dye from the polyester fibers;

2. removing the excess of the dye-containing dye-stripping solvent which is not absorbed by the fibers and fabrics;

3. contacting the fibers (which many contain residual dye-stripping solvent) with sufficient addition of a primary dissolution solvent under selective dissolution conditions for polyester fibers;

4.   removing the undissolved fibers or the other
impurities from the solution; and

5.   separating the solvent or solvents from the
polyester by evaporating the solvent from the
dissolved and/or molten polyester without
precipitating the polyester from solution.

It is significant and important to point out that none of these recovery

methods disclose or suggest any steps or detailed recovery procedures for

nylon.   Rather, they are limited to specific dissolution techniques for

recovery of the unrelated polymer, polyester.   In another U.S. Patent

Number 4,064,079 (Sidebotham et al) a modified polyester recovery

method is disclosed which does not include a step for removal of dye from

the polyester fibers.

U.S. Patent Number 5,240,530 and 5,288,349 (Fink) teach a carpet

recycling and recovery method in which portions of the carpet are initially

ground and melted for a feedstock. Carpets containing different types of

materials are ground mechanically so that the contained fiber length is reduced between 1/4" and 1/16". These fibers are then separated in an aqueous bath on the basis of specific gravity. Neither of these patents teach or suggest separating nylon fibers from polyester fibers by subjecting the mixed fibers to water and then heat, that is, there are no extraction steps disclosed.

U.S. Patent Number 5,294,384 (David et al) discloses a method for converting waste carpet material into a thermoplastic composition. As starting material, the carpet samples (waste) may have any pile weight and also may be comprised of non-homogeneous mixtures of components. The samples are melt blended with or without a compatibilizer in a temperature range of from 250 degrees Celsius to about 260 degree Celsius and at a pressure of from about 350 to 450 psi and a shear rate of about 200-400/sec.; most preferably this step is carried out in a twin screw extruder. The blends thus formed may then be palletized or processed into other commercially acceptable forms. Blend compositions which are disclosed include mixtures of nylon, polyolefins, SBR latex, and inorganic fiber. Using the method described in this patent no attempt is made (no steps included) to separate the fiber mixture into their consistent parts or

fractions; rather, the mixtures are merely transformed into a different mixture having a different form from the starting components.

In U.S. Patent Number 5,370,757 (Corbin et al) a carpet product is disclosed which has two distinct sections, a top section constructed entirely from nylon (Nylon 6) and a bottom section. The top section is thus easily removable from the bottom section for replacement thereof without any damage to the bottom section. After such removal, the top section can then be recycled to e-Caprolactum for re-use in Nylon 6 carpet or it can be used in other Nylon 6 products.

Further, U.S. Patent Number 5,342,854 (Serod) describes a method for separating and recovering polyester from polyester/cotton blends. The polyester/cotton materials is cut and chopped into small pieces and then dried. These dried scraps are placed into a vessel containing a sulfone solvent such as an alkyl sulfone having from 1 to 10 carbon atoms and heated to 150 degrees Celsius. This mixture is steeped (with agitation) for about 90 minutes at this temperature. Thereafter, the temperature of the mixture is raised to 190 degrees Celsius and maintained thus for about another 35 minutes. The solvent containing polyester is then separated for further treatment to precipitate the recovered polyester. There are no

methods or steps described for separating the polyester from any other polymeric systems or other polymeric fibers.

U.S. Patent Number 5,198,471 does not teach a process related to this invention. There is no disclosure of nylon fibers, carpet, or any of the solvents. In U.S. Patent Number 3,696,058 (Tate) a process is disclosed for recovering solid scrap thermoplastic polymers such as polyamides and polyesters. The process comprises the following steps:

    a.   dissolving said thermoplastic polymer in hexafluorisopropanol;

    b.   filtering said polymer solution;

    c.   mixing the polymer solution with an excess of water at temperature of from 60 to 100 degrees Celsius; and

    d.   separating the precipitated polymer from the water, wherein the thermoplastic polymer is selected from the group consisting of polyamide, polyester, polyacrylonitrile and polyacetal.

In this patent the solvents employed for the polymer are fluoroalcohols. It has been known to use formic acid and sulfuric acid as well as various types of solvents such as for instance ethylene glycol, propylene glycol, meta-cresol and various tri-glycerides and fatty acids to dissolve nylons polymeric materials as a step in producing cast polyamide fibers including nylon fibers.

SUMMARY of the INVENTION

It is an objective of this invention to provide a recycling process for carpeting material containing nylon polymers and/or nylon fibers.

It is also an objective to describe processes for separating and recovering plastic and polymer components of carpeting, used carpets, carpets scraps and the like including mixtures of synthetic carpeting materials one or more components or portions of which contain nylon. Another objective is to provide an economical, practical and environmentally acceptable method for recovery of components from carpeting materials containing nylon polymers.

Another specific objective is to recover Nylon 6 and Nylon 6,6 from nylon containing carpet scraps and used carpeting.

A further object is to separate and recover nylon polymer from carpeting containing other polymers such as polyesters, polyamides, P.E.T. (poly-ethylene terepthtalate) and other polymers as well as natural fibers.

Another object is to provide an efficient recycling process for nylon containing carpeting materials or any other material containing nylon. Other objectives will be disclosed in the detailed description of the invention process described herein below.

DESCRIPTION of the INVENTION

At present there are a number of different but related reasons and objectives which make carpet recycling of prime importance.

There are both environmental and economic reasons for the drive with respect to recycling processes and methods. Practical and economic values are advantageous for limiting landfill usage for the old and discarded carpeting as well as otherwise useless carpeting scraps.

Recycling generally can include methods for reprocessing or reconditioning for reuse as such, conversion of the carpeting or the components thereof into a new or different product which may have a different and often less demanding or more generic application, or use of one or more processes or process steps in a way which recovers all or part of the value of the components.

In the processes of this invention, a number of these advantages and objectives are achieved.

This invention broadly relates to the recycling and recovery of products from carpeting in which the fibers contain at least substantial quantities of nylon as well as polyester and P.E.T. (poly-ethylene terephthalate). In addition, acrylic fibers may be present as well as various olefinic resins. Also, in some instances, natural fibers such as cotton and/or wood may also be present.

The carpeting, which is subjected to recycling, also has a backing material which may be for instance polypropylene, polyethylene, acrylic resin, a straw-burlap material known commercially as "JUTE", a mixture of these with possibly other materials in smaller amounts.

It is also commonly required that some kind of "gluing" agent or adhesive be present at least in a minor amount in order to attach and securely bind the fibers to the backing. The adhesive during the recovery process becomes part of the inert by-product stream and thus remains a part of the inert fraction.

The process of this invention can be advantageously and quite satisfactorily practiced with any carpet as the starting material, provided only that there is some nylon fibers present. The nylon can be of the type known commercially as Nylon 6 (poly-6-aminocaproic acid), Nylon 6,6 (poly-hexamethyleneadipamide), Nylon 8 (poly-8-aminocaprylic acid), Nylon 11 (poly-11-aminoundecanoic acid), and Nylon 6,10 (poly-hexamethylene sebacamide).

It is not necessary, or at least not practical or highly effective to separate the carpet fibers from the backing that is, because the release of the adhesive from the fibers during the recovery step are effectively accomplished. It is not generally necessary to remove the adhesive as whatever remains with the fiber will remain as a solid residue in the separation step.

In one embodiment of the invention, the ground carpeting, preferably primarily comprising the nylon containing fibers are admixed with a selective solvent. This solvent must be appropriately selected and is preferred to be a glycolic compound (polyhydric alcohol) such as ethylene glycol or propylene glycol or glycerol and can also be various mixtures of these solvents. This solvent may also be an organic formate, such as methyl or ethyl formate, hydrochloric acid, formic acid, methanol, nitric acid, glacial acetic acid, fluorinated alcohols, m-cresol, phenolic compounds, chloroform-methanol, methanol-lithium chloride, potassium thiocyanate, benzyl alcohol, butane diol 1,1, dimethyl sulfoxide, triethylene glycol, and tetraethylene glycol.

It has been found by actual testing and experimentation that glycerol is the most effective solvent and is preferred for isolation and recovery of the nylon components in the fibers. It is found to be the most environmentally friendly solvent of those listed.

The basis for the separation of the types of nylon fractions (Nylon 6 and Nylon 6,6) is the relative solubility of the two types in the solvent depending on the temperature. Thus, the different types can be identified, separated and removed by varying the temperature. The Nylon 6 fraction

is soluble in glycerol at 155 degrees Celsius whereas the Nylon 6,6 is soluble at 195 degrees Celsius, all the nylon polymers will be dissolved. Then the mixture is cooled and the Nylon 6,6 will not be soluble and can be separated and removed as a solid. Further cooling to about 150 degrees Celsius will cause the Nylon 6 to separate and it can be removed as a solid.

The process can also be carried out by selective heating of the fibers in solution. At a temperature of about 150 degrees Celsius and the Nylon 6 will be dissolved and can then be separated with the glycerol and the Nylon 6,6 is thus the remaining solid which has not been heated to a sufficiently high temperature to dissolve.

The nylon which is recovered as a solution in glycerol or other organic solvent can be easily recovered by precipitation upon cooling followed by washing with water where as the solid nylon polymer separates from the liquid solution.

The many advantages include the ability to separate the nylon polymers from other polymers, adhesives and fibers, using a safe environmentally acceptable steps to recover clean, relatively pure nylon polymers. Although advantage is that there is a relatively simple,

economical and effective step which is readily included to separate Nylon 6 and Nylon 6,6 and recover both in a pure form.

The following Examples are typical processes for the recovery of the products according to the invention but are in no way intended to limit the invention process and products thereto.

EXAMPLES

Example 1.

This process and the steps thereof relate to the recovery of nylon, particularly Nylon 6,6 both from home and commercial carpets. Carpet containing Nylon 6,6 is dissolved in a hot, highly pure glycerol at elevated temperatures. At high temperatures, nylon oxidizes with oxygen and/or hydrolysis with water. To prevent oxidation various stabilizers may be added to the solvent. Alternatively, working under a nitrogen environment renders an effective protection against nylon degradation from both oxidation and hydrolysis.

Upon dissolution, the solution is quickly withdrawn to a dry vessel where it is quickly cooled to 40 degrees Celsius or lower. The solution is

washed with water to remove traces of glycerol, then filtered, and lastly dried under vacuum at 40 to 60 degrees Celsius to recover the nylon polymer. The following is an example of the method used in practicing this recovery and recycling process:

1. 1200 ml of pure glycerol is heated to and maintained at 205 C and 1 ATM. of pressure in a stirrer equipped vessel where it is uniformly stirred at a moderate speed.

2. Meanwhile, a constant stream of nitrogen gas is applied to the solvent as it heats up to purge out any residual oxygen.

3. 100 grams of Dupont Stainmaster carpet is added to the hot solvent.

4. The initial carpet fiber is sample and found to be Nylon 6 with a relative viscosity of 1.7.

5.   15 minutes after all the nylon is dissolved, the solution is pumped out of the heating vessel via a heated 0.25 inch diameter stainless steel pipe into a dry flask that is sitting in an ice bath.

6.   When the solution cools down to 40 C or below it is washed with water at a ratio of 20:1 by volume and filtered, for the final wash.

7.   For the final wash potassium iodine (KI) is added to the water as a heat stabilizer for future processing.

8.   The final solution is filtered and the cake is dried in an oven purged with nitrogen then under vacuum allowed to dry at 45 C for three days.

9.   The final material is checked for its purity and relative viscosity (RV). The final material exhibited an increase in relative viscosity to 2.21.

Example 2.

This process and the steps thereof relate to the recovery of Nylon 6 and Nylon 6,6 both from home and commercial carpets.

Carpet containing Nylon 6 and Nylon 6,6 is dissolved in a hot, highly pure glycerol at elevated temperatures. To prevent oxidation stabilizers are added to the solvent. Alternatively, working under a nitrogen environment renders an effective protection against nylon degradation. Upon dissolution at 165 C, the solution containing Nylon 6 is quickly withdrawn to a dry vessel while the undissolved residue containing Nylon 6,6 is dissolved in a second vessel at 200 C and withdrawn into its dry clean vessel. The two nylon containing vessels are cooled quickly to 40 C. The solid particles are washed independently of each other to remove any trace of glycerol. The polymer is then filtered and dried under vacuum at 40 to 60 C to recover the pure nylon polymer. The polymer is then checked for relative viscosity and purity using differential scanning calorimetry. The Nylon 6,6 and Nylon 6 exhibited a single melting peak confirming the melting point of the pure components proving the polymer separation was performed accurately.

CLAIMS:

1. Process for recycling of waste carpeting and waste carpeting containing materials which comprises multiple separation steps using selective solvents under controlled temperature conditions which steps include selective stepwise separation and recovery of carpet backing, adhesives, and individual types and compositions of fibers present.

2. The process of Claim 1 for recycling and recovery of products from waste carpeting which includes as preliminary steps the reduction of the waste carpeting to granular, particulate form followed by treatment to remove inert solids and non-fibrous fillers.

3. The process of Claim 1 in which the waste carpeting and waste carpeting containing materials contain substantial amounts of nylon fibers which are separated and recovered as fibers or polymer.

4. The process of Claim 1 in which the waste carpeting contains substantial amounts of nylon fibers and substantial amounts of at least one other fiber which is substantially separated from the nylon fibers, and each polymer fiber composition, as recovered, suitable for polymer reuse.

5. The process of Claim 4 in which at least one of the fibers other than nylon fiber is a synthetic polymer fiber.

6. The process of Claim 5 in which at least one of the synthetic fibers other than nylon is a polyester.

7. The process of Claim 5 in which at least one of the synthetic fibers other than nylon is a polyamide.

18

8.   The process of Claim 5 in which at least one, of the fibers other than nylon is a terephthalate polymer.

9.   The process of Claim 4 in which at least one of the fibers other than nylon is natural fiber.

10. The process of Claim 1 in which the selective solvent employed for separation of the nylon fiber fraction comprises at least substantial percentages of at least one polyhydric alcohol used at preselected, controlled temperatures from which the nylon is subsequently separated by controlled temperature variation.

11. The process of Claim 1 in which the Nylon 6 is separated from Nylon 6,6 by preselected variation and control of temperatures and time of treatment of a polyhydric alcohol solvent.

12. The process of Claim 10 in which the selective solvent is glycerol.

13. The process of Claim 10 in which the selective solvent is ethylene glycol.

14. The process of Claim 10 in which the selective solvent is propylene glycol.

15. The recovered nylon polymer obtained by the recycling steps for carpeting as described in Claim 1.

19

CZECHOSLOVAKIAN PATENT NO. 143,502

Application Date: November 17, 1969

Application No.:   PV 7534-69

Int. Cl.:   C 07 d 41/06

UDC: 547.486.3-318

Application Announced: May 31, 1971

Date of Publication: November 15, 1971

METHOD FOR PRODUCING CAPROLACTAM

Inventors: Kamil Petrů, Milan Hajas,
                            and Vladimír Kaláb, all
                            of Žilina

Patent Holder: The right to use this
                            patent belongs to the
                            State under Act 34/1957
                            Zb., §3, paragraph 6.

The invention relates to a method for producing caprolactam from waste consisting of a mixture of polycaprolactam and a nonpolyamide component. Such waste materials arise during the processing of old tires containing polycaprolactam cords, for example, during the manufacture and processing of filled or laminated polycaprolactam, in the manufacture and processing of textiles from mixed fibers, and elsewhere. They cannot be incinerated, and several of the materials require special

decontamination procedure. The invention solves the problem of utilizing such wastes in an economically efficient way, and the goal of the invention is to allow them to be processed commercially into a high-quality, valuable product.

The nonpolyamide component of the waste materials, which are not water-soluble, differs depending on the origin of the waste. The nonpolyamide component cannot be separated from the polycaprolactam by mechanical grinding and classification.

Because of the chemical nature of the nonpolyamide component, or because of the high proportion it constitutes in the waste, the wastes are not suitable for utilization by known methods for treating wastes consisting solely of polycaprolactam. When direct thermal depolymerization to caprolactam is used, large quantities of residue remain in the reactor, and the resulting product is contaminated by the breakdown products of the nonpolyamide component; in the case of thermal depolymerization by steam, only dilute solutions of polycaprolactam are obtained. Considering the high energy requirements and the low yields of caprolactam, direct depolymerization is not economically efficient.

A method for dissolving polyamide in sulfuric acid was developed for utilizing waste resulting from regeneration of old tires. After the solution as filtered, the polycaprolactam was obtained by precipitating it out with water; the precipitate was dried and polycaprolactam was obtained in the form of a powder. This powder is used for molding applied coatings or is converted to granulated form. Wastes of other origins also can be processed to a polycaprolactam powder using polycaprolactam solvents other than sulfuric acid. A disadvantage of all these

approaches is the unsatisfactory quality of the powdered
polycaprolactam obtained, which results from the degradation
processes that operate during the dissolution of the
polycaprolactam and from the impossibility of washing the
precipitate completely clean. The resulting powder always has a
lower molecular weight than the original polycaprolactam and
always contains undesirable admixtures. On standing, it rapidly
turns brown and forms a crumbly coating that adheres poorly to
substrates. When melted, it produces a brownish granular
material and items molded from it or fibers spun from it are of
inferior quality.

It has now been found that such waste materials can be
utilized economically for processing into a high-quality product
by the method according to the invention, namely, by first
dissolving waste mixtures of polycaprolactam and a nonpolyamide
component in water or a polycaprolactam solvent. Dissolution in
water is accomplished under elevated pressure at the melting
point of polycaprolactam. According to alternative versions of
the invention, all known polycaprolactam solvents can be used.
Dissolution is accomplished at ordinary or elevated temperature
depending on the type of solvent used. If the required
temperature is above the boiling point of the solvent, the
dissolution is accomplished under elevated pressure. Dissolution
can be accomplished at ordinary temperatures when sulfuric acid,
hydrochloric acid, phosphoric acid, formic acid, acetic acid,
tricresol, or other solvents that dissolve polycaprolactam at
ordinary temperatures are used. Dissolution can be accomplished
at elevated temperatures without excess pressure with ethylene
glycol, glycerin, dimethyl sulfoxide, methanolic or ethanolic

solutions of resorcinol, or calcium chloride or other solvents that dissolve polycaprolactam at temperatures higher than the temperatures but lower than their boiling points. Dissolution can also be accomplished at elevated temperatures without excess pressure using caprolactam, phenol, or other solvents that dissolve polycaprolactam at temperatures above their melting points but below their boiling points.

Dissolution can be accomplished at elevated pressure and elevated temperature with methanol, ethanol, or other solvents that dissolve polycaprolactam at temperatures above their boiling points. Dissolution can also be accomplished using suitable mixtures of solvents.

The nonpolyamide component is separated from the resulting polycaprolactam solution by filtering it through a suitable filtering device, preferably located in the bottom of the dissolution vessel. The type of filtering device depends on the particle size of the nonpolyamide component. It could be a perforated bottom or a wire screen, for instance. The nonpolyamide component retained by the filter is removed mechanically or by rinsing it off with the solvent used for the dissolution, and can be utilized further in some way depending on its nature. For example, particles of rubber or fiberglass can be used in construction as thermal insulation.

The polycaprolactam, in the form of a solution or suspension, is sent either directly or following removal of the solvent to thermal decomposition.

A suspension of polycaprolactam forms spontaneously on cooling, or on cooling accompanied by the loss of excess pressure when water or polycaprolactam was used for the dissolution.

These solvents do not introduce any chemically foreign substances into the depolymerization process, and the actual depolymerization process can also be accomplished in their presence. The process can also be accomplished, however, with these solvents being regenerated in the first phase by distillation. The suspension may also appropriately be conveyed directly to the depolymerization step when methanol or ethanol was used as the solvent, since these solvents also can be regenerated easily by distillation in the first phase of the depolymerization process.

If an organic or inorganic acid was used as the solvent, the polycaprolactam must first be isolated from the solution by precipitating it out with water or alcohol and separating it from the liquid phase by sedimentation, filtration, or centrifugation before it is sent on to be depolymerized. Since the waste acids in the liquid phase can be regenerated or decontaminated only with difficulty, the use of organic or inorganic acids as solvents is less desirable.

If ethylene glycol, glycerin, or dimethyl sulfoxide was used as the solvent, they can be removed from the resulting suspension by centrifugation, filtration, evaporation, extraction, or by another known means, and the polycaprolactam is then sent to thermal decomposition. The regenerated solvent can be reused in the dissolution step.

The thermal decomposition of polycaprolactam is accomplished by known methods, appropriately employing catalysts and superheated steam. The charge can consist of polycaprolactam obtained by the method described alone, or polycaprolactam in a mixture with other wastes of unfilled polycaprolactam. The

depolymerized product can be processed alone or together with the main stream of ordinary caprolactam produced by known methods to give the final product.

The advantage of the invention consists in the more economical utilization of waste relative to known methods in the form of powdered polyamide, since in conjunction with depolymerization, the method according to the invention can produce high-quality caprolactam, thus allowing for the utilization of polyamide waste on the commercial scale.

The subject matter of the invention is illustrated but not limited by the following examples:

Example 1

1 kg of waste from the production of polyamide laminate consisting of 70% polycaprolactam and 30% fiberglass was heated with 10 kg of water in an autoclave fitted with a metal screen. At 320°C the pressure in the autoclave was 23 kPa/cm². After one hour the resulting melt was discharged to a depolymerization reactor heated to 275°C. 2.5 g of H_3PO_4 and 2.5 g of H_3BO_3 were added to the melt as a mixed depolymerization catalyst, and the resulting monomeric caprolactam was distilled with steam superheated to 400°C. A 17% aqueous solution of caprolactam was obtained. After being condensed to a 92% solution it was cooled to 10°C and yielded 480 g of caprolactam and 170 g of mother liquor. A one-step distillation gave a final caprolactam with a

permanganate number of 6700 sec and volatile bases equivalent to 0.1 mL of 0.01N H_2SO_4 per 100 g of caprolactam. The mother liquor was recycled back to caprolactam production.

Example 2

1 kg of waste from the processing of old tires consisting of 60% polycaprolactam cord and 40% rubber was heated with 10 kg of ethylene glycol in a dissolving vessel with an outlet fitted with a metal screen. After being heated for six hours at 180°C, the resulting solution was discharged to a cooling vessel; after the solution had cooled to 60°C, polycaprolactam spontaneously precipitated out, forming a fine suspension. 8.3 kg of ethylene glycol were recovered from this suspension on a centrifuge, and polycaprolactam was isolated in the form of a fine paste which, after being washed with water, was conveyed to a depolymerization reactor. 3 g of H_3BO_3 were added to the paste as a depolymerization catalyst, and the temperature was gradually raised to 275°C. The resulting monomeric caprolactam was distilled with steam superheated to 400°C. An 18.5% aqueous solution of caprolactam was obtained. This was mixed with a 1% addition of activated carbon for adsorption [of impurities]. After the adsorbent was completely removed, the aqueous solution was condensed to 65% caprolactam and extracted three times with trichloroethylene. The caprolactam was extracted from the trichloroethylene into water and the aqueous extract was vacuum condensed and vacuum distilled with an addition of 0.5% NaOH. The yield was 34 g of the first fractions, 32 g of the last

fractions, and 416 g of final caprolactam. The final caprolactam had a permanganate number of 16,800 sec and contained volatile bases equivalent to 0.80 mL of 0.01N H_2SO_4 per 100 g of caprolactam.

Example 3

1 kg of textile waste consisting of 53% polycaprolactam fiber and 47% cotton fiber was heated with 10 kg of methanol at 130°C and a simultaneous pressure off 8.8 kPa/cm² in an autoclave in which the outlet was fitted with a metal screen. After one hour the resulting solution was discharged to a depolymerization reactor, where polycaprolactam spontaneously precipitated out and 6.7 kg of methanol spontaneously distilled off. As the resulting suspension of polycaprolactam was heated gradually to 275°C, 3.2 kg of methanol were distilled from it. To the polycaprolactam melt there were then added 5 g of H_3PO_4 as a depolymerization catalyst, and the resulting monomeric caprolactam was distilled with steam superheated to 400°C. The yield was a 15% aqueous solution of caprolactam that was condensed to give a concentration of 65% caprolactam, which was then extracted three times with trichloroethylene. After the caprolactam had been extracted from the trichloroethylene into water, the aqueous extract was vacuum condensed and vacuum distilled with an addition of 0.5% NaOH. The yield was 20 g of the first fractions, 20 g of the last fractions, and 390 g of

final caprolactam. The final caprolactam had a permanganate number of 10,590 sec and contained volatile bases equivalent to 1.20 mL of 0.01N H_2SO_4 per 100 g of caprolactam.

Claims

1. A method for obtaining caprolactam from waste mixtures of polycaprolactam and a nonpolyamide component, characterized in that wastes are brought into contact with water or a polycaprolactam solvent, with the dissolved caprolactam being separated from the nonpolyamide component and sent on, either directly or after preliminary removal of the solvent, to be thermally depolymerized, where monomeric caprolactam is regenerated, for example by steam.

2. A method as in Claim 1 characterized in that a solution of polycaprolactam in a solvent or a suspension of polycaprolactam in solvent is sent directly to be depolymerized, and the solvent is regenerated by distillation or is driven off with steam.

3. A method as in Claim 1 characterized in that the solvent is removed from the polycaprolactam, for example by centrifuging, filtration, extraction, or evaporation, prior to the depolymerization step.

Crystalline Transitions in Powders of Nylon 66 Crystallized from Solution

HOWARD W. STARKWEATHER, JR. and GLOVER A. JONES, *E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898*

Synopsis

Powders of nylon 66 were crystallized from solution in methanol and in other solvents. These powders exhibit a latent heat of about 4.5 cal/g at the Brill transition near 200°C where the unit cell changes from a triclinic to a pseudohexagonal form. The dimensions of the hydrogen-bonded sheets are almost unchanged up to 240°C, but the separation between the sheets increases with increasing temperature. Above 245°C, the interchain separation increases rapidly, and permits the powder to be extruded in an essentially plastic manner to form coherent extrudates. As the temperature of treatment is increased above 245°C, the latent heat of the Brill transition is reduced toward zero, the heat of fusion is reduced from about 30 cal/g to about 20 cal/g, and an endotherm at 261°C is replaced by one at 267°C.

INTRODUCTION

In 1942, Brill[1] reported that the two strongest peaks in an x-ray diffraction pattern from nylon 66, the (100) reflection and the (010,110) doublet, merge into a single peak at 160°C. He also stated that in the presence of water vapor, the transformation occurred at 140°C. In later work,[2] Brill related the phenomenon to the thermosetting of filaments.

The Brill transition, as it has come to be known, represents a change from a triclinic unit cell to a pseudohexagonal form. In the latter cell, the c axes and the polymer chains are still tilted with respect to the ab plane, but the projection of the unit cell on a plane normal to the c axis is metrically hexagonal. The temperature of the transition has been reported variously from 100 to 240°C,[3–7] and it appears to be sensitive to the crystallization, annealing, and deformation history of the sample. There have been reports of a small latent heat associated with the Brill transition,[8,9] but its thermodynamic properties have not been well defined.

In earlier work,[10] it was found that nylon 66 having an unusually high degree of crystallinity could be obtained by crystallization from methanol under autogeneous pressure. It was decided to use similar samples in effort to learn more about the Brill transition.

PREPARATION OF POWDERS

Zytel® 101 nylon molding pellets (15 g) and methanol (250 g) were charged to a 400 ml stainless-steel shaker tube. The tube was flushed with nitrogen, sealed, heated to 180°C for 20 min, and cooled with continuous shaking. The maximum pressure recorded during the experiment was 420 psig. The product, a fine

powder, was separated from the liquid by filtration and dried overnight in a vacuum oven at 96°C with a nitrogen bleed. Unless otherwise stated, this is the material used in subsequent experiments. Scanning electron microscopy revealed aggregated globules 100–200 μm in diameter with surface dendrites 0.3–2 μm wide. Low-angle x-ray diffraction showed a peak corresponding to a spacing of 64 Å. This is equivalent to a fold period of five repeat units assuming chain folding on (001) planes.

In other runs, as much as 53.5 g of nylon was dissolved in 250 ml of methanol to give similar powders. Runs with 15 g of nylon were also done at temperatures from 140 to 160°C. While only fine powder was formed at 160 and 180°C, mixtures of fine powder and undissolved pellets were recovered from runs at 140 and 150°C. When water was substituted for methanol, fine powder was formed at 200–300°C, and undissolved pellets were recovered from runs at 160 and 180°C.

In order to avoid elevated pressure, a number of high boiling solvents were tried at a concentration of 5 g of nylon per 100 g of solvent. These are listed in Table I in the order of decreasing solubility parameter. None of the solvents having solubility parameters below 12 dissolved nylon 66 at or below their boiling points, except triethylene glycol and tetraethylene glycol; and in these cases the dissolution temperatures were very high.

The powders prepared from high boiling solvents appeared to be quite similar to those precipitated from methanol. Methanol, which has a solubility parameter of 14.5, was preferred because its volatility reduces the retention of solvent during drying.

DIFFERENTIAL SCANNING CALORIMETRY

Scans obtained with a Du Pont differential scanning calorimeter (DCS) calibrated according to the manufacturer's instructions at a heating rate of 20°C/min are shown in Figure 1. A peak near 100°C due to absorbed water can be eliminated by a preliminary run to 140°. There is a broad endotherm with a peak

TABLE I
Precipitation of Nylon 66 from High Boiling Solvents

| Solvent	Solubility parameter	Boiling point (°C)	Dissolution temperature (°C)	Precipitation temperature (°C)
Glycerol	16.5	290d	200	180
Ethylene glycol	14.6	198	174	140
Propylene glycol	12.6	189	175	140
Benzyl alcohol	12.5	205	185	110
Butane diol-1,4	12.1	235	185	140
Diethylene glycol	12.1	245	205	161
Dimethyl sulfoxide	12.0	189	160	141
Cyclohexanol	11.4	162	did not dissolve	
Dimethyl acetamide	10.8	165	did not dissolve	
Dimethyl phthalate	10.7	282	did not dissolve	
Triethylene glycol	10.7	276	260	185
n-Octyl alcohol	10.3	194	did not dissolve	
Diphenyl ether	10.1	259	did not dissolve	
Tetraethylene glycol	9.9	328	262	210
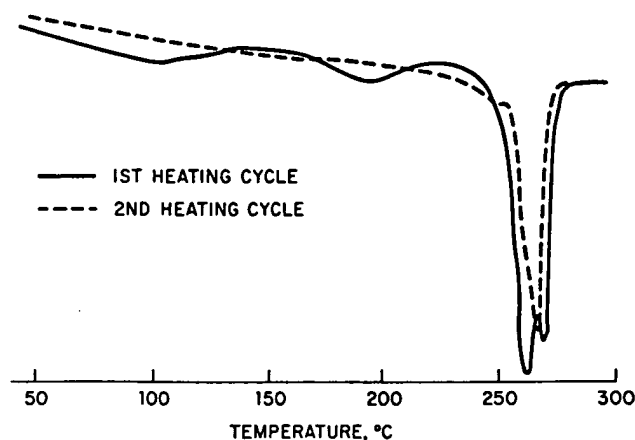
Fig. 1. DSC scans for nylon powder: (——) first and (- - -) second heating cycles.

near 200°C having a latent heat of 4.5 cal/g. This peak is associated with the Brill transition and is unchanged in subsequent cycles provided the sample has not been heated above 240°C. Melting peaks occur at 262 and 270°C with a combined heat of fusion of 26.6 cal/g. Preheating at 225–265°C produces a new peak at 267°C which is the sole melting peak in a second heating cycle after melting and cooling. This melting point is in line with earlier reports on unoriented polymer crystallized from the melt.[3,11,12] Lower melting points have been reported for oriented fibers.[13,14] The 200°C peak is absent in the second cycle.

The effect of a preliminary heating cycle terminating at selected temperatures between 240 and 270°C on the heats of transition is shown in Figure 2. As the preheating temperature is increased, the latent heat of the transition at 200°C decreases to zero, and the heat of fusion decreases from about 30 cal/g to about 20 cal/g. These effects both begin near 245°C and are complete at about 267°C. Near this temperature, the endothermal peak at 261°C is replaced by one at 267°C. The heat of fusion for samples heated above 267°C or crystallized from the melt is close to literature values for drawn fibers.[14] The decline in the heat of fusion of solution-crystallized powders between 245 and 267°C is reminiscent of an earlier study of melt-crystallized films.[3] In that case, the crystallinity increased with increasing annealing temperatures up to 250°C but decreased on annealing between 255°C and the melting point followed by rapid quenching.

In studies on unoriented chips and oriented bristle of nylon 66, Khoury[15] observed that positive spherulites disappeared at a temperature which varied between 250 and 256°C. Between 250 and 265°C, negative spherulites grew following the disappearance of the positive spherulites. The optical melting point of the negative spherulites were 268–270°C.

Powders prepared from the solvents listed in Table I gave very similar DSC scans. The temperature of the Brill transition peak was 199 ± 4°C, and its latent heat was 4.6 ± 0.6 cal/g. Melting peaks occurred at 261.5 ± 1.0 and 269.5 ± 1.8°C, and the heat of fusion was 28.3 ± 1.3 cal/g.

The effect of heating rate on the temperatures of the endothermal peaks is shown in Figure 3. A double melting peak was seen only at rates up to 20°C/min, and the temperature of the upper peak was independent of rate. Extrapolation to zero heating rate gave the following values. The peak associated with the Brill
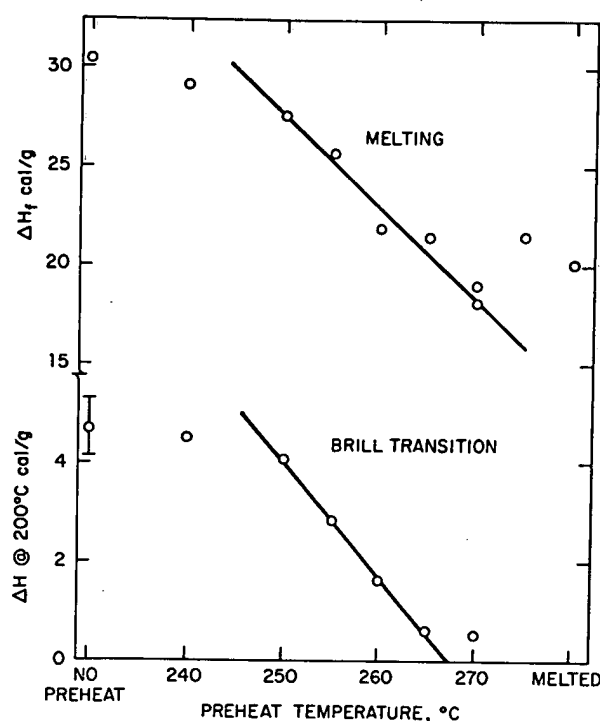
Fig. 2. Effect of preheating on heats of transition.

transition occurs at 194°C with a latent heat of 4.55 cal/g.   The melting peaks are at 258 and 270°C, and the heat of fusion is 28 cal/g.

In studies on fibers exhibiting two melting peaks, the lower temperature peak which, as in our case, moved to higher temperatures with increasing heating rates was attributed to the transformation from one form to another.[13,14]
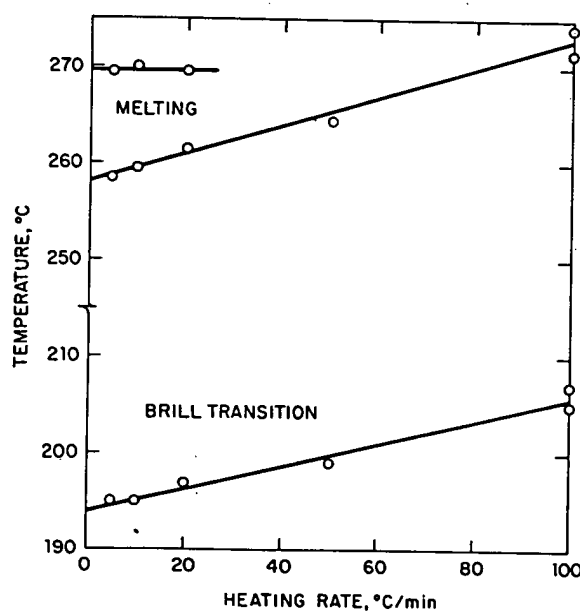

Fig. 3. Effect of heating rate on the temperatures of endothermal peaks.

UNIT CELL PARAMETERS

X-ray diffraction scans were obtained with a Rigaku θ–θ Diffractometer using Cu $K\alpha$ radiation. This instrument, in which the sample remains horizontal, is especially useful for studies on fluids. Digital data were taken at intervals of 0.05° in 2θ. The counting time was varied as needed to define the positions of the peaks. The 2θ scale was calibrated with diamond and cobalt oxide. The temperature was measured by a thermocouple embedded in the sample. There was good agreement between transition temperatures determined by x-ray diffraction and differential scanning calorimetry.

Bunn and Garner[16] reported that at room temperature nylon 66 has a triclinic unit cell with a density of 1.24 ± 0.04 g/cm^3 and the following parameters:

$$a = 4.9 \text{ Å} \qquad \alpha = 48.5°$$
$$b = 5.4 \text{ Å} \qquad \beta = 77°$$
$$c = 17.2 \text{ Å} \qquad \gamma = 63.5°$$

The number of peaks observed in x-ray diffractometer scans from powders crystallized from solution is much greater than from unoriented melt-processed samples. Data taken from a powder sample at 24°C are compared with values calculated from a least-squares refinement in Table II. The intensity data of Bunn and Garner[16] were used to index the reflections. The calculated unit cell has a density of 1.213 ± 0.006 cm^3. This compares favorably with the densities of 1.220 ± 0.002 g/cm^3 reported by Starkweather and Moynihan[10] and 1.210 ± 0.005 g/cm^3 reported by Haberkorn and co-workers,[17] based on extrapolation of an amorphous band in the infrared spectrum to zero absorbance. Crystals of this density have been estimated to have a heat of fusion of 56 cal/g.[17] The parameters for this cell are

TABLE II
X-Ray Diffractometer Data Taken at 24°C from a Powder of Nylon 66 Precipitated from Methanol

hkl	2θ Calc.	Obs.	hkl	2θ Calc.	Obs.
001	6.89	6.65	020	49.17	49.65
002	13.80	14.20	220	49.17	
100	20.27	20.30	237	52.94	
101	20.67		$\bar{1}$27	53.13	53.1
111	20.97	21.25	217	53.48	
003	20.76		210	57.20	
010	24.01	24.08	310	57.20	56.7
110	24.01		107	56.56	
$\bar{1}$11	34.97	35.05	037	56.92	
0$\bar{1}$2	34.91		$\bar{1}$20	62.09	
017	38.19		217	61.23	61.75
$\bar{1}$10	37.86	38.05	207	62.24	
210	37.86		207	70.63	
200	41.22		$\bar{1}$37	70.64	71.05
117	41.19	41.05	227	71.11	
027	41.20		030	77.23	76.9
$\bar{1}$17	45.92	45.80	330	77.23	
			410	80.21	80.5

melting peaks

:perature peak
ς heating rates
3,14

:aks.

$$a = 4.97 \pm 0.01 \text{ Å} \qquad \alpha = 48.35 \pm 0.3°$$
$$b = 5.47 \pm 0.02 \text{ Å} \qquad \beta = 76.6 \pm 0.3°$$
$$c = 17.29 \pm 0.07 \text{ Å} \qquad \gamma = 62.5 \pm 0.2°$$

Changes in the diffraction angles for the principal reflections with temperature below 200°C, are shown in Table III. These data were taken on a sample of powder which had been annealed at 240°C to stabilize the structure without producing the changes depicted in Figure 2. The parameters of the hydrogen-bonded sheets are essentially unchanged between 24 and 183°C and have the following values: $a = 4.96$ Å, $c = 17.34$ Å, and $\beta = 77.3°$.

Above 200°C, the structure is pseudohexagonal. The unit cell is triclinic, and the two-dimensional projection on a plane normal to the c axis is metrically hexagonal. The (001) and (002) reflections are changed very little, and this indicates that the c axis is still tilted with respect to the ab plane. The separation between the hydrogen-bonded sheets has increased to the point where the two strong reflections indexed as (100) and (010,110) merge to form a single strong sharp reflection.

The properties of the pseudohexagonal unit cell are most simply expressed in terms of the following restrictions on the reciprocal lattice parameters: $a^* = b^*$ and $\gamma^* = 120°$.

Instead of the six parameters generally needed to define a triclinic cell, only four reciprocal lattice parameters are needed for a pseudohexagonal cell: $a^* = 1/d_{100}$, $c^* = 1/d_{001}$, α^*, and β^*.

Diffraction data taken at 202 and 240°C are given in Table IV together with the calculated unit cell parameters. Indexing is based on the intensity data of Colclough and Baker.[18] There is little change over this temperature range except for a continued increase in α. The angle β within the hydrogen bonded sheet is a few degrees larger than it was below 200°C, but the interchain separation within the hydrogen bonded sheet, $a \sin\beta$, is almost unchanged. The contraction

TABLE III
X-Ray Data Measured below 200°C on Nylon 66 Powder Annealed at 240°C

Temperature (°C)	24	120	154	183
hkl		2θ		
001	6.6	6.75	6.6	6.7
002	13.5	14.05	13.7	13.6
100	20.2	20.4	20.5	20.6
010,110	24.0	23.6	23.0	22.25
015			26.6	26.6
017	37.8	37.8	37.55	37.9
117,027	41.0	41.1	41.15	40.95
$\bar{1}$17	46.0			
020,220	49.6	48.4		45.5
1,3,14	76.9			
Unit cell parameters				
a (Å)	4.95 ± 0.05	4.96 ± 0.5	4.95 ± 0.07	4.97 ± 0.05
b (Å)	5.44 ± 0.04	5.54 ± 0.07	5.57 ± 0.09	5.73 ± 0.08
c (Å)	17.38 ± 0.04	17.35 ± 0.09	17.29 ± 0.10	17.36 ± 0.08
α (deg)	48.3 ± 0.5	48.9 ± 0.8	50.6 ± 1.0	51 7 ± 1.0
β (deg)	76.6 ± 0.6	76.8 ± 1.4	78.0 ± 1.6	77.9 ± 1.5
γ (deg)	62.6 ± 0.5	62.1 ± 1.0	61.9 ± 1.4	60.9 ± 1.0
Volume (Å³)	308 ± 2.5	315 ± 3	323 ± 3	336 ± 1
Density (g/cm³)	1.219 ± 0.010	1.193 ± 0.010	1.165 ± 0.012	1.117 ± 0.005

with temperature
1 on a sample of
structure without
of the hydrogen-
°C and have the

ll is triclinic, and
xis is metrically
ttle, and this in-
The separation
it where the two
n a single strong

mply expressed
ice parameters:

iclinic cell, only
hexagonal cell:

V together with
ntensity data of
ure range except
n bonded sheet
hain separation
The contraction

it 240°C

183

6.7
13.6
20.6
22.25
26.6
37.9
40.95

45.5

4.97 ± 0.05
5.73 ± 0.08
17.36 ± 0.08
51 7 ± 1.0
77.9 ± 1.5
60.9 ± 1.0
336 ± 1
1.117 ± 0.005

TABLE IV
X-Ray Data on Nylon 66 Powder in the Pseudohexagonal Form

| Temperature (°C) | 202 | | 240 | |
hkl	2θ obs.	2θ calc.	2θ obs.	2θ calc.
001	6.65	6.50	6.60	6.49
002	13.25	13.01	13.25	13.01
100,010,110	21.05	21.14	21.00	21.09
$\bar{1}03$		26.05		26.05
114	26.05	26.05	26.05	26.05
004		26.20		
210,$\bar{1}$10,120	37.10	37.05	37.00	36.80
Unit cell parameters				
a (Å)		4.92 ± 0.02		4.93 ± 0.02
b (Å)		6.04 ± 0.10		6.03 ± 0.09
c (Å)		17.23 ± 0.25		17.18 ± 0.23
α (deg)		53.5 ± 1.2		57.8 ± 1.1
β (deg)		80.7 ± 0.6		80.7 ± 0.5
γ (deg)		60.5 ± 0.5		60.4 ± 0.03
Volume (Å³)		351 ± 5		352 ± 5
Density (g/cm³)		1.069 ± 0.015		1.067 ± 0.014

of the c dimension at elevated temperatures which has been reported for melt-crystallized samples[7,18] appears not to occur with the powder crystallized from solution.

Above 240°C, only the $(00l)$ and the $(hk0)$ reflections remain, and the unit cell parameters can no longer be calculated. It is possible, however, to determine the interchain separation from

$$a \sin\beta = b \sin\alpha = d_{100}/\sin\gamma^*$$

The interchain separations are plotted against temperature in Figure 4. The interchain separation within the hydrogen bonded sheets, $a \sin\beta$, increases only slightly from room temperature to 250°C. The interchain separation between the hydrogen-bonded sheets, $b \sin\alpha$, increases sharply approaching the Brill transition where the two separations become equal in the pseudohexagonal structure.

Between 250°C and the final melting point, there is another sharp increase in the interchain separation. This is the region of the first melting transition shown in Figures 1 and 3. Annealing in this temperature range eliminates the endotherm near 200°C and reduces the heat of fusion (Fig. 2).

RHEOLOGY AND DYNAMIC MECHANICAL PROPERTIES

It is possible to extrude the powder with a capillary rheometer at temperatures from 260 to 270°C. The dependence of shear stress on apparent shear rate is shown in Figure 5. At 260 and 265°C, the rheological exponent, the slope of a log–log plot of shear stress versus apparent shear rate, is 0.41 at low shear rates. At higher shear rates, the rheological exponent becomes 0.17 at 260°C and is essentially zero at 265°C. A zero exponent is equivalent to plastic behavior. Low exponents have been observed for the extrusion of highly crystalline poly-(tetrafluoroethylene) below its melting point and for crystalline and smectic states of certain low molecular compounds.[19] At 270°C, the rheological exponent
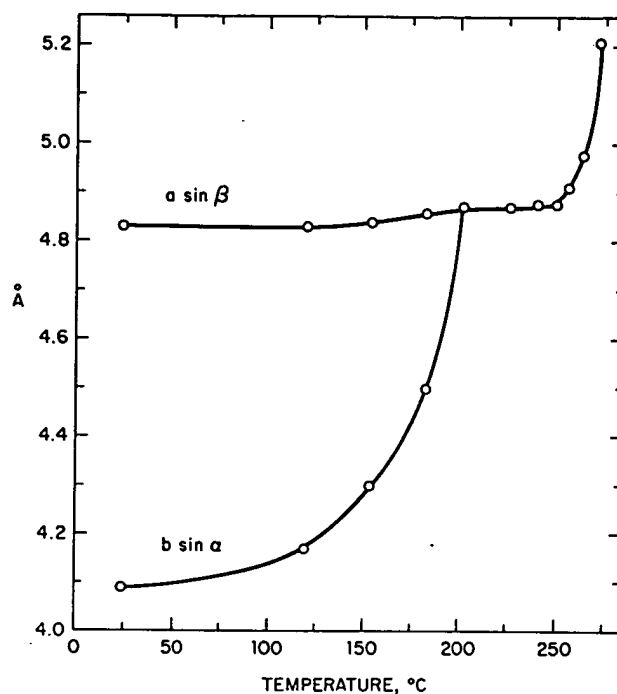
Fig. 4. Dependence on temperature for the interchain separations in crystals of nylon 66.

is 0.72 over a wide range of apparent shear rates.   The apparent viscosities vary from 10^3 to 10^7 poise.

DSC scans from extrudates prepared at 260–270°C differed from those from samples which had merely been heated to those temperatures.   The extrudates
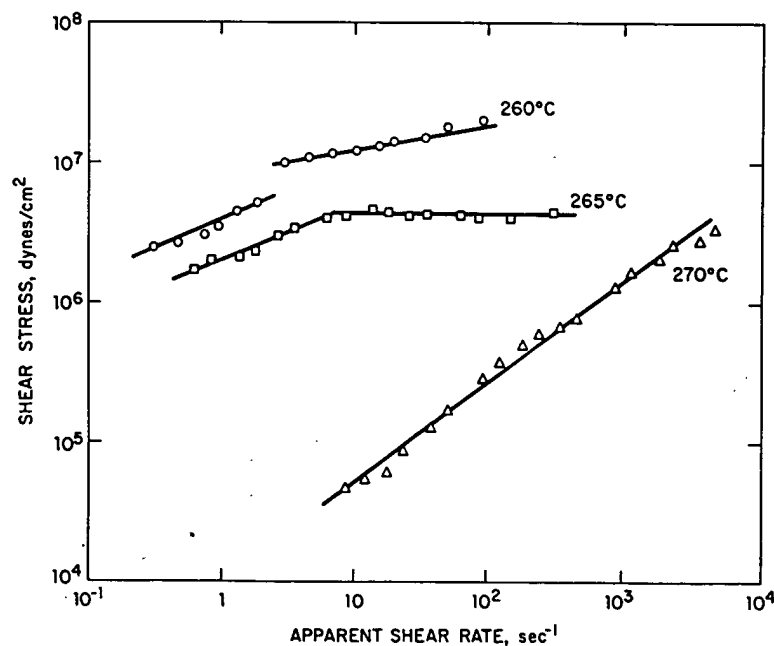

Fig. 5. Rheological data below the melting point.

retained a Brill transition with a latent heat of about 2.5 cal/g. The melting peak temperatures were higher, and in extrudates prepared at 265–270°C, there was an additional melting peak at 282°C. This may indicate that some of the crystallites were changed to a more chain-extended form. Both the extrudates and the powders annealed at the same temperatures had heats of fusion near 20 cal/g.

Coherent extrudates were obtained with both cylindrical and rectangular dies. Our rectangular die had a cross section of 0.050 × 0.250 in., a straight-section length of 0.500 in., and a 45° conical inlet. The rectangular extrudates were run on the Du Pont dynamic mechanical analyzer.[20,21] The flexural modulus and the loss tangent for a powder extrudate prepared at 260°C and an injection molded specimen are compared in Figures 6 and 7. Both samples had been dried in a vacuum oven at 110°C. The temperature of the α relaxation near 80°C is about 20° higher in the powder extrudate. The heights of the α and γ loss peaks are similar, reflecting similar levels of crystallinity as indicated by the heats of fusion, 20.1 cal/g for the powder extrudate and 18.6 cal/g for the injection molding. However, the modulus of the powder extrudate was higher at temperatures between the α-relaxation and the Brill transition. This is thought to be due to a more perfect crystalline order in the powder crystallized from solution.
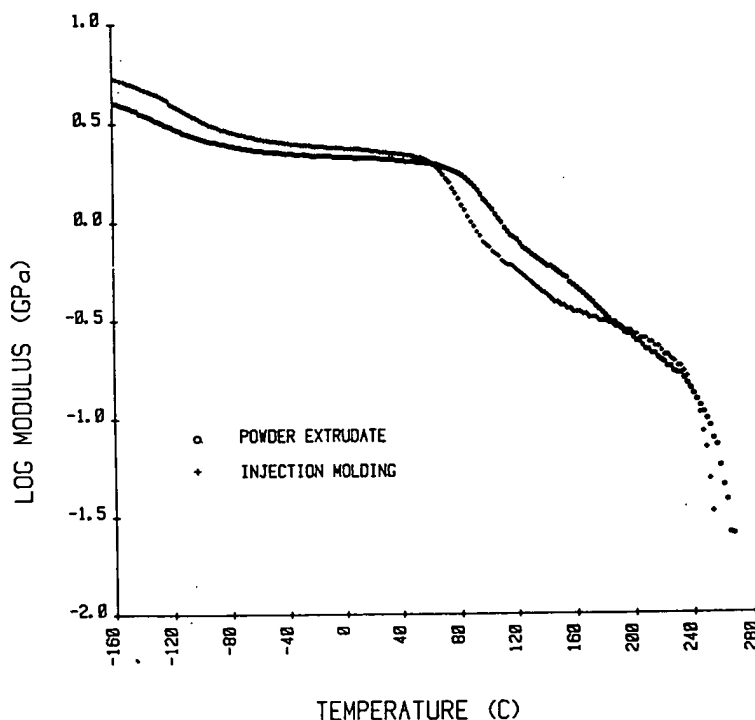

Fig. 6. Flexural modulus measured with a Du Pont dynamic mechanical analyzer: (O) powder extrudate; (+) injection molding.
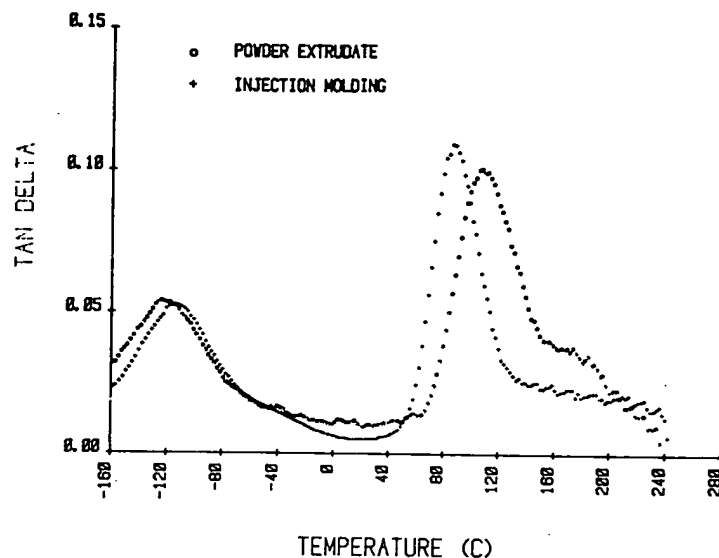
Fig. 7. Loss tangent measured with a Du Pont dynamic mechanical analyzer. Symbols as in Figure 6.

CONCLUSIONS

The endotherm near 200°C in powders crystallized from solution indicates clearly that the Brill transition is thermodynamically first order. The dimensions within the hydrogen-bonded sheets are essentially constant over a wide range of temperature.

Heating at temperatures above 245°C produces a number of interesting changes. The latent heat of the Brill transition is gradually reduced toward zero, and the heat of fusion is also reduced. An endothermal peak at 261°C is replaced by one at 267°C. In this temperature range, the interchain separation increases rapidly. The decrease in the number of peaks in the x-ray diffraction pattern suggests increased motion within the crystals. These changes permit the powder to be extruded in an essentially plastic manner.

References

1. R. Brill, *J. Prakt. Chem.*, **161**, 49 (1942).
2. R. Brill, *Makromol. Chem.*, **18/19**, 294 (1956).
3. H. W. Starkweather, J. F. Whitney, and D. R. Johnson, *J. Polym. Sci., Part A*, **1**, 715 (1963).
4. J. H. Dumbleton and B. B. Bowles, *Text. Res. J.*, **36**, 933 (1966).
5. A. Anton, *J. Appl. Polym. Sci.*, **12**, 2117 (1968).
6. J. H. Dumbleton and T. Murayama, *Kolloid Z. Z. Polym.*, **238**, 410 (1970).
7. T. Itoh, *Jpn. J. Appl. Phys.*, **15**, 2295 (1976).
8. P. W. Allen, *Research (London)*, **5**, 492 (1952).
9. R. C. Wilhoit and M. Dole, *J. Phys. Chem.*, **57**, 14 (1953).
10. H. W. Starkweather and R. E. Moynihan, *J. Polym. Sci.*, **22**, 363 (1956).
11. M. J. Kohan, *Nylon Plastics*, Wiley, New York, 1973, p. 308.
12. *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, p. III-67.
13. J. P. Bell, P. E. Slade, and J. H. Dumbleton, *J. Polym. Sci., A-2*, **6**, 1773 (1968).

14. G. E. Sweet and J. P. Bell, *J. Polym. Sci., A-2,* **8,** 1273 (1972).

15. F. Khoury, *J. Polym. Sci.,* **33,** 389 (1958).

16. C. W. Bunn, and E. V. Garner, *Proc. R. Soc. (London), Ser. A,* **189,** 39 (1947).

17. H. Haberkorn, K. H. Illers, and P. Simak, *Polym. Bull.,* **1,** 485 (1979); also *Colloid Polym. Sci.,* **257,** 820 (1979).

18. M. L. Colclough and R. Baker, *J. Mater. Sci.,* **13,** 2531 (1978).

19. H. W. Starkweather, *J. Polym. Sci. Polym. Phys. Ed.,* **17,** 73 (1979).

20. R. L. Blaine and L. Woo, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.,* **17,** 1 (1976).

21. R. M. Ikeda and H. W. Starkweather, *Polym. Eng. Sci.,* **20,** 321 (1980).

288

mbols as in Figure

tion indicates
he dimensions
: a wide range

of interesting
d toward zero,
°C is replaced
tion increases
iction pattern
ait the powder

es refinements of

, *Part A,* **1,** 715

New York, 1975,

968).